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C2C 1652 215 220 22Y 250 252 25Y 281 30Y 313 31Y 321 322 323 32Y 338 342 34Y 364 36Y 450 453 45Y 595 598 602 610 634 63X 640 644 650 660 662 670 680 699 774 775 AA KY LH NE
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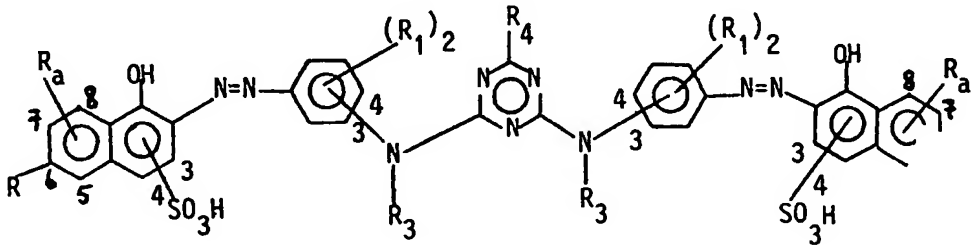
(56) Documents cited
None

(58) Field of search
C4P

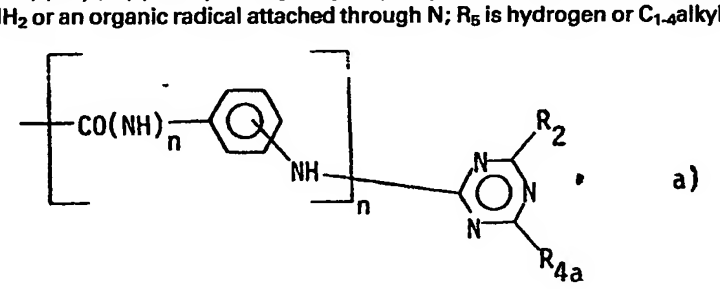
(54) Basic and cationic triazinyl disazo dyes

(57) New dyes of formula I and their metal complexes impart red to blue shades to cellulose, polyamids, polyester, and polyacrylonitrile fibres and textiles, and to paper, leather and bast fibres.



(I)

where R is hydrogen, SO_3H or NR_5R_6; R_a is hydrogen or NR_5R_6; provided that one of R and R_a is NR_5R_6; R_1 is hydrogen, halogen, OH C_{1-4}alkyl, C_{1-4}alkoxy or SO_3H; R_3 is hydrogen or C_{1-4}alkyl; R_4 is halogen, OH, C_{1-4}alkyl, C_{1-4}alkoxy, phenyl, $-NH_2$ or an organic radical attached through N; R_5 is hydrogen or C_{1-4}alkyl; and R_6 is a radical of formula (a) or (b):



a)

wherein *n* is 0 or 1; *m* is 1-4; R_2 and K_a are each substituents attached through N; and R_{4a} is defined as R_4.

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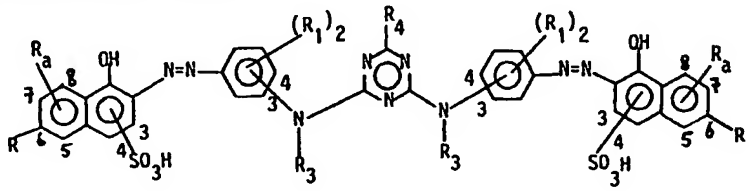
SPECIFICATION

Improvements in or relating to organic compounds

The invention relates to sulpho containing basic azo compounds for use in dyeing.

The invention provides compounds, in metal-free, 1:1 metal complex or 1:2 metal complex form and in free acid or acid addition salt form, of formula I



where each R independently is hydrogen, SO_3H or NR_5R_6 and each R_a independently is hydrogen or NR_5R_6 provided that R and R_a on the same naphthyl group are not both the same; that one of R and R_a on the same naphthyl group is $-NR_5R_6$; and when R is SO_3H R_a on the same naphthyl ring is in the 8-position;

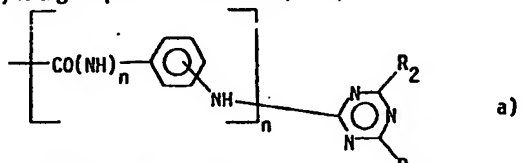
each R_1 independently is hydrogen, halogen, OH, C_{1-4}alkyl, C_{1-4}alkoxy or SO_3H;

each R_3 independently is hydrogen or C_{1-4}alkyl;

R_4 is halogen, OH, C_{1-4}alkyl, C_{1-4}alkoxy, phenyl, $-NH_2$, an aliphatic, cycloaliphatic, aromatic or heterocyclic amine which may contain 1 to 3 heteroatoms; or a hydrazine group; in which the N-atom of the amine or hydrazine group is attached to the C-atom of the triazinyl group and the amine or hydrazine group can bear protonatable basic groups and/or quaternary N-atoms;

each R_5 independently is hydrogen or C_{1-4}alkyl;

each R_6 independently is a group of the formula a) or b)



a)

$-CO(CH_2)_{\overline{m}}K_a$ (b)

where each n independently is 0 or 1 and each m independently is 1, 2, 3 or 4;

R_2 is an aliphatic, cycloaliphatic, aromatic or heterocyclic amine or hydrazine group in which the N-atom is attached to the C-atom of the triazinyl group and the amine or hydrazine group can bear protonatable basic groups and/or quaternary N-atoms;

R_{4a} has a significance of R_4 independent of R_4

Ka is $N(R_7)_2$; $-\overset{\oplus}{N}(R_8)_2R_9\,A^{\ominus}$; $-\overset{\oplus}{N}(R_8)_2-A-N(R_7)_2\,A^{\ominus}$ or $\overset{\oplus}{N}(R_8)_2-A-N(R_8)_2R_9\,2\,A^{\ominus}$

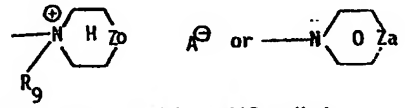
where each R_7 independently is hydrogen; unsubstituted C_{1-6}alkyl; C_{2-6}alkyl substituted by one of OH, CN and halogen; phenyl C_{1-3}alkyl, the phenyl group of which is unsubstituted or substituted by 1 to 3 substituents selected from halogen, C_{1-4}alkyl and C_{1-4}alkoxy; or C_{5-6}cycloalkyl unsubstituted or substituted by 1 to 3 (C_{1-4})alkyl groups or

both R_7's together with the N-atom to which they are attached form a five- or six-membered saturated heterocyclic ring containing one to three heteroatoms;

each R_8 independently has a non-cyclic or cyclic significance of R_7 except hydrogen; and

each R_9 independently is C_{1-4}alkyl unsubstituted or substituted by one of phenyl, $-CONH_2$ and unsubstituted cyclohexyl or C_{2-4}alkyl substituted by one of OH, halogen and CN; or C_{3-6}alkenyl or $-(CH_2)_2-CO(C_{1-4}$alkyl);

or both R_8's and R_9's together with the N-atom to which they are attached form a group of the formula



where Z_o is $-O-$, a direct bond, $-CH_2-$; $-NH-$, $-NC_{1-4}$alkyl;

$-\overset{\oplus}{N}(C_{1-4}\text{alkyl})_2\,A^{\ominus}$; $-SO_2-$, $-SO-$, $-S-$; or $-N-(CH_2)_{2-3}NH_2$;

Za is a direct bond or $-CH_2-$;

or a heterocyclic amine, unsubstituted or substituted by 1 to 3 C_{1-4}alkyl groups;

each A independently is C_{1-12}alkylene uninterrupted or interrupted by 1 to 3 heteroatoms; or unsubstituted C_{3-8}alkenylene; and

$A^{\ominus}$ is a non-chromophoric anion;

with the provisos:-

i) that the sum of cationic and protonatable basic groups exceeds the sum of sulpho and anionic groups by at least one; and

ii) that the sulpho groups on the naphthyl groups are in the 3- or 4-position (shown);

iii) that the $-NR_3$ groups on the phenyl rings are in the 3- or 4-position (shown)

iv) that when both R's are $-NR_5R_6$, both R_6 s are a group of formula a) and both n s are zero then both $-NR_3$ groups are in the 3-position (shown) on the phenyl rings.

For the avoidance of doubt the invention includes mixtures of one or more compounds of formula I above.

Preferably when one or both R_6's are a group of formula a) and n=0 then R_2 and R_{4a} are not piperazine.

Where any symbol appears more than once in a formula unless indicated to the contrary its significances are independent of one another.

Any alkyl, alkylene or alkenylene present is linear or branched unless indicated otherwise. The alkyl group of any alkoxy group is linear or branched unless indicated to the contrary.

In this specification halogen means fluorine, chlorine, bromine or iodine, preferably chlorine.

In this specification any alkyl is preferably C_{1-4}alkyl, more preferably methyl or ethyl, most preferably methyl and any alkoxy is preferably C_{1-4}alkoxy, more preferably methoxy or ethoxy, most preferably methoxy.

Any sulpho group present may be in free acid or salt form. When in salt form the $-SO_3^{\ominus}$ is balanced by a cation $M^{\oplus}$ (where $M^{\oplus}$ is a non-chromophoric cation for example $Na^{\oplus}$, $K^{\oplus}$ or $NH_4^{\oplus}$) or by a protonated basic non-cationic group or by a cationic group in the molecule.

Unless otherwise indicated the preferred significance of a variable applies to that variable regardless of where the variable is set forth in the specification.

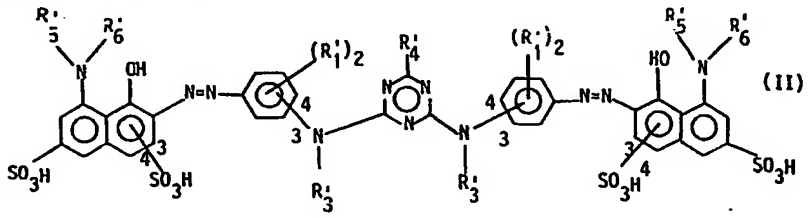
Any aliphatic amine group is preferably a mono-C_{1-4}alkyl- or di-(C_{1-4}alkyl)-amine group; each alkyl group independently is unsubstituted or substituted by 1 to 3 substituents selected from halogen, phenyl, hydroxy or C_{5-6}cycloalkyl, preferably unsubstituted or mono substituted by phenyl or hydroxy, any hydroxy being other than in the α-position.

Any cycloaliphatic amine group present is preferably C_{5-6}cycloalkylamine, the cycloalkyl group of which may be substituted by one or two C_{1-2}alkyl groups.

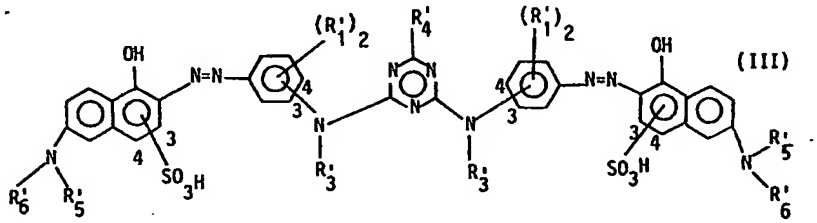
Any aromatic amine group present is preferably aniline, the phenyl ring of which is unsubstituted or substituted by one to three substituents selected from C_{1-4}alkyl, C_{1-4}alkoxy, halogen, hydroxy and phenoxy.

Any heterocyclic amine present is preferably a pyridine, (when unsaturated) or a morpholine, pyrrolidine, piperidine, piperazine group (when saturated). Each group may be substituted by one to three C_{1-4}alkyl groups.

Preferred compounds of formula I are those in metal-free 1:1 or 1:2 metal complex form or in free acid or acid addition salt form of formulae II or III



(II)



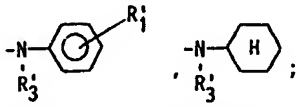
(III)

in which

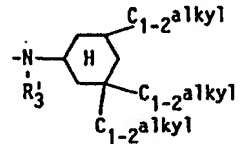
R_1' is hydrogen, Cl, Br, CH_3, OCH_3 or SO_3H

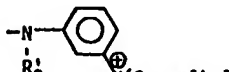
R_3' is hydrogen or CH_3;

R_4' is Cl, Br, $-NH_2$, $-CH_3$, $-OH$, phenyl, OCH_3,



mono(C_{1-4}alkyl)amino, di(C_{1-4}alkyl)amino, monohydroxy C_{2-4}alkylamino, bis-(hydroxyC_{2-4}alkyl)amino;

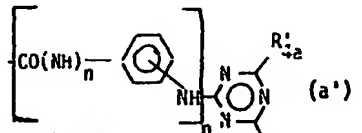




or R_2' defined below;

R_5' is hydrogen, methyl or ethyl;

R_6 is



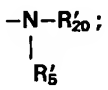
(a')

or $-CO(CH_2)_{m'}-K_a'$ (b')

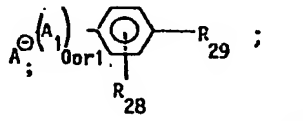
where m' is 1, 2 or 3;

R_{4a}' has a significance of R_4' independent of R_4'

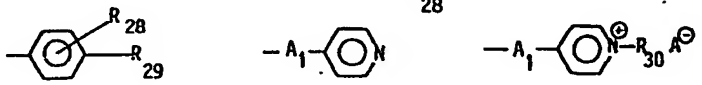
R_2' is

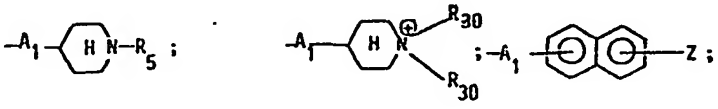


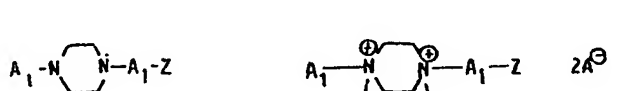
where R_{20}' is C_{1-12}alkyl, unsubstituted or substituted by one $-OH$ and uninterrupted or interrupted by one to three groups selected from $-N(R_7)-$ and $-\overset{\oplus}{N}(R_8)_2\,A^{\ominus}$; $-NHCOCH_2-Z$; $-CH_2CONH-A_1-Z$; $-A_1-Z$;

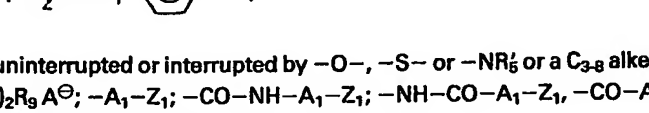


or









where

A_1 is a C_{1-8}alkylene uninterrupted or interrupted by $-O-$, $-S-$ or $-NR_5'$ or a C_{3-8} alkenylene group;

Z is $-N(R_7)_2$; $-\overset{\oplus}{N}(R_8)_2R_9\,A^{\ominus}$; $-A_1-Z_1$; $-CO-NH-A_1-Z_1$; $-NH-CO-A_1-Z_1$, $-CO-A_1-Z_1$; $-SO_2-NH-A_1-Z_1$ or $-NHNHCOCH_2-Z_1$;

R_{28} is halogen, $-OH$, $-NO_2$, $\oplus$ C_{1-4}alkyl or C_{1-4}alkoxy;

R_{29} is a group $-N(R'_7)_2$ or $-N(R'_8)_2R'_9\,A^{\ominus}$ or a group $-CO-A_2-Z_1$, $-NHCO-A_2-Z_1$, $-CONH-A_2-Z_1$, $-SO_2NH-A_2-Z_1$; $-A_2-Z_1$ or $-NHNHCOCH_2-Z_1$;

A_2 is C_{1-8}alkylene;

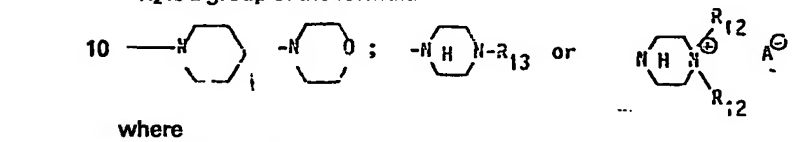
R_{30} is C_{1-4} alkyl;

Z_1 is $-N(R'_7)_2$ or $-\overset{\oplus}{N}(R_8)_2R_9\,A^{\ominus}$

where

R'_7, R'_8 and R'_9 are defined below; or

R'_2 is a group of the formula



where

R_{12} is C_{1-4}alkyl;

R_{13} is hydrogen or C_{1-4}alkyl unsubstituted or substituted by $-NH_2$;

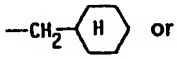
K'_a is $N(R'_7)_2$; $-\overset{\oplus}{N}(R'_8)_2R'_9\,A^{\ominus}$; $-\overset{\oplus}{N}(R'_8)_2-A-N(R'_7)_2\,A^{\ominus}$ or $-\overset{\oplus}{N}(R'_8)_2A-\overset{\oplus}{N}(R'_8)_2R'_9\,2A^{\ominus}$

R'_7 is hydrogen, linear or branched C_{1-4}alkyl, linear hydroxyC_{2-3}alkyl, 2-cyanoethyl, 2-chloroethyl or phenyl (C_{1-3}alkyl), the phenyl group of which is unsubstituted or substituted by 1 to 3 substituents selected from Cl, CH_3 or OCH_3;

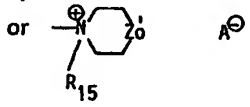
or both R'_7 together with the N-atom to which they are attached form an unsubstituted morpholine, piperidine, pyrrolidine, piperazine or N-methylpiperazine group;

R'_8 has a non-cyclic or a cyclic significance of R'_7 other than hydrogen; and

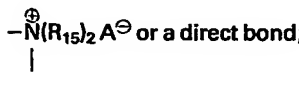
R'_9 is methyl, ethyl, propyl, cyanoethyl, hydroxyethyl, chloroethyl, benzyl, $-CH_2-CH=CH_2$, $-CH_2-CO-CH_3$, $-CH_2CONH_2$ or



both R'_8s and R'_9 together with the N-atom to which they are attached form unsubstituted pyridine, picoline, lutidine or



where R_{15} is methyl or ethyl and Zó is $-CH_2-$, $-O-$, $-NH-$,



with the provisos

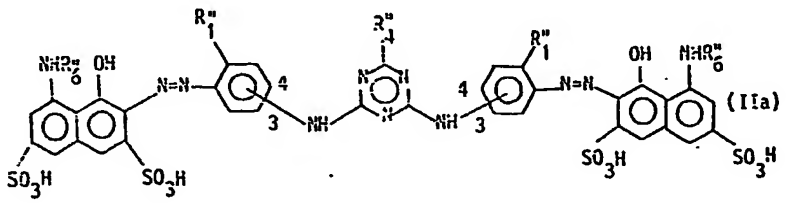
i) that in the compounds of formulae II and III the sum of the cationic and protonatable basic groups exceeds the sum of sulpho groups and anionic groups by at least one; and

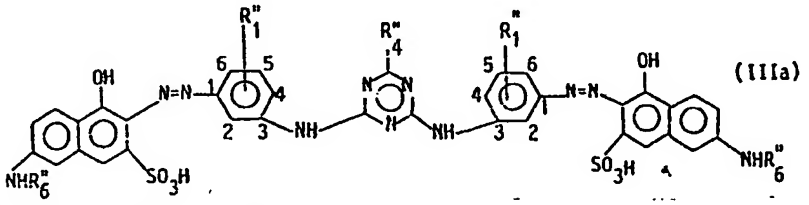
ii) that in the compounds of formulae II and III the floating sulpho groups on the naphthyl groups are in the 3- or 4- position (shown);

iii) that in the compounds of formulae II and III the floating $-NR'_3$ groups are in the 3- or 4-position (shown); and

iv) that in the compounds of formula III when both R_6's are a group of formula a' and both n's are zero, then both $-NR'_3$ groups are in the 3-position on the phenyl groups and R'_2 and R'_{4a} are not piperazine.

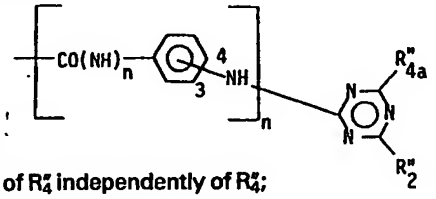
More preferred compounds of formula I are those, in metal-free, 1:1 metal complex or 1:2 metal complex form or in free acid or acid addition salt form, of formula IIa or IIIa



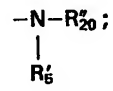


(IIIa)

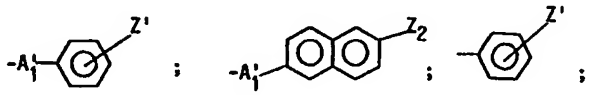
in which R''_1 is hydrogen, methyl, $-SO_3H$ or OCH_3;
R''_4 is Cl, NH_2, CH_3, OCH_3, OH, $-N(C_2H_4OH)_2$ $-NHC_2H_4OH$ or R''_2 (defined below);
R''_6 is a group of the formula

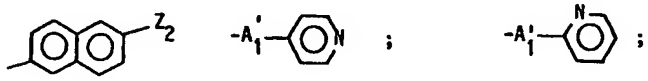


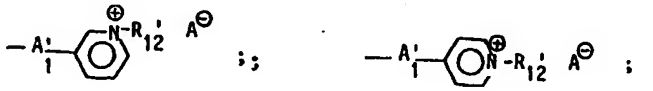
or is $-CO-(CH_2)_{m''}-K''_a$;
where m'' is 1 or 2;
R''_{4a} has a significance of R''_4 independently of R''_4;
R''_2 is

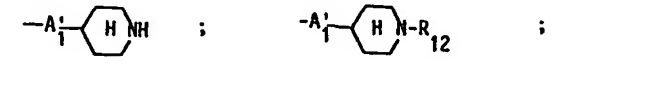


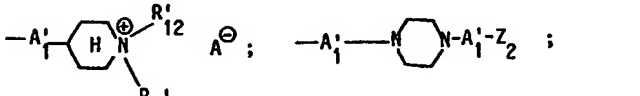
where R''_{20} is a group of the formula $-(CH_2)_{2-3}-N(R''_7)-(CH_2)_{2-3}-NR''_7R'_{12}$; $-(CH_2)_{2-3}-\overset{\oplus}{N}(R''_8)_2-(CH_2)_{2-3}-\overset{\oplus}{N}(R''_8)_2R'_{12}\,A^{\ominus}$; $-(CH_2)_{2-3}-N\,R''_7\,R'_{12}$; $-(CH_2)_{2-3}-\overset{\oplus}{N}(R''_8)_2\,R'_{12}\,A^{\ominus}$; $-NHCOCH_2-Z_2$; $-CH_2CONH-A'_1-Z_2$; $-A'_1-Z_2$;

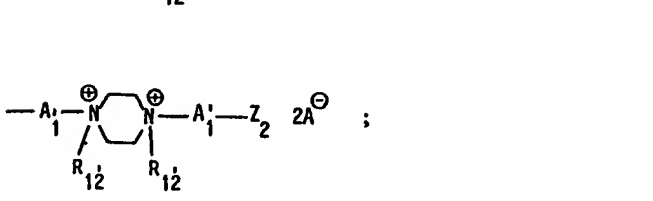




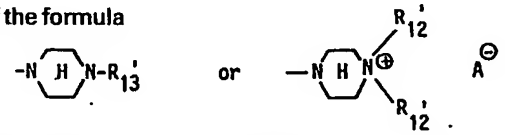








or R_2'' is a group of the formula



where

A_1' is C_{1-8}alkylene uninterrupted or interrupted by $-O-$, $-S-$ or

Z' is $-N(CH_3)_2$, $-\overset{\oplus}{N}(CH_3)_3\,A^{\ominus}$; $-CONH-A_1'-Z_2$; $-SO_2NH-A_1'-Z_2$; $-A_1-Z_2$; $-NHNHCOCH_2-Z_2$ or $CO-A_1'-Z_2$;

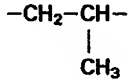
R_{12}' is methyl or ethyl;

R_{13}' is hydrogen, methyl or $-C_2H_4NH_2$;

Z_2 is a group $-N(R_7'')_2$ or $-\overset{\oplus}{N}(R_8'')_2R_9''\,A^{\ominus}$;

K_3'' is a group of formula $-N(R_7'')_2$; $-\overset{\oplus}{N}(R_8'')_2-A_3-\overset{\oplus}{N}(R_7'')_2$ $-\overset{\oplus}{N}(R_8'')_2-A_3-\overset{\oplus}{N}(R_8'')_2R_9''\,2\,A^{\ominus}$; $-\overset{\ominus}{N}(R_8'')_2R_9''\,A^{\ominus}$;

A_3 is $-CH_2)_s$; $-(CH_2)_2-N(CH_3)-(CH_2)_2-$; $-CH_2-C(CH_3)-CH_2-$ or



where s is an integer from 2 to 6 inclusive;

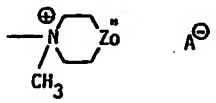
R_7'' is hydrogen, methyl or ethyl (more preferably methyl or ethyl) or

both R_7''s together with the N-atom to which they are attached form an unsubsituted morpholine, piperidine, pyrrolidine, piperazine or N-methyl piperazine ring.

R_8'' is methyl or ethyl; and

R_9'' is methyl, ethyl or benzyl; or

both R_8''s, R_9'' and the N-atom to which they are attached form a pyridine or picoline group (attached by the N-atom) or a group of formula



where Z_o'' is $-NH-$, $-O-$, $-CH_2-$, $-\overset{|}{N}(CH_3)-$ or $-\underset{\oplus}{\overset{|}{N}}(CH_3)_2\,A^{\ominus}$

with the provisos:

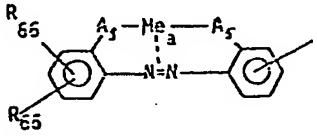
i) that the sum of cationic and/or protonatable basic groups is greater than the sulpho and anionic groups present by at least one;

ii) that R_2'' and R_{4a}'' are not piperazine, and

iii) that R_1'' in the compounds of formula IIIa is in the 4- or 6-position shown.

Preferred metallisable groups are $-NH_2$, $-OH$ or $-O(C_{1-4}alkyl)$ which are situated ortho to an azo bridge on a benzo or a phenyl group. Metallisation of such groups can be represented below:

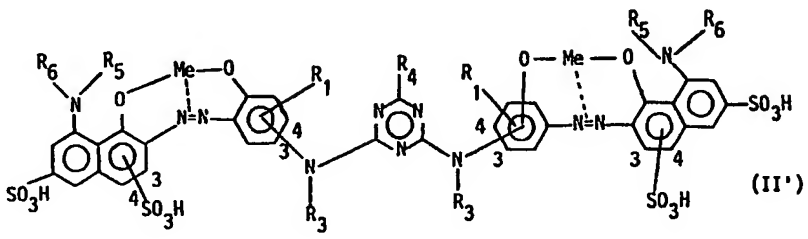
or



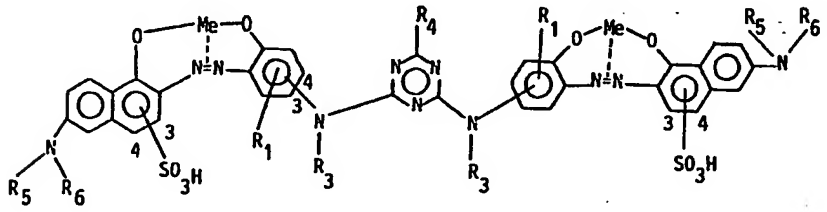
in which each A_5 independently is $-O-$ or $-NH-$;

Me_a is a 1:1 or 1:2 metal complex forming metal both R_{66}'s are ortho to each other and together form an aromatic ring system (for example together with the two carbon atoms to which they attached form a

Preferred compounds of formula I in metallised form are those in free acid or acid addition salt form of formula II' or III'



(II')



(III')

where the symbols R_1, R_3- R_5 and R_6 are as defined above and M_3 is a 1:1 or 1:2 complex forming metal atom with the provisos that:

i) in the compounds of formula II' and III' the sum of cationic and protonatable basic groups exceeds the sum of sulpho and anionic groups by at least one;

ii) in the compounds of formula II' and III' the floating sulpho groups are in the 3- or 4-position (shown);

iii) in the compounds of formulae II' and III' the floating groups

are in the 3- or 4-position (shown);

iv) in the compounds of formula III' when both R_6s are the groups of formula a) and n is zero then the NR_3 groups are in the 3-position (shown).

Preferably Me is copper, chromium, cobalt, nickel or manganese when a 1:1 complex forming metal and is chromium, cobalt, iron or nickel when a 1:2 complex forming metal;

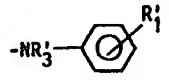
In the above formulae:

R_1 is preferably R_1';
R_2 is preferably R_2', more preferably R_2'';
R_3 is preferably R_3';
R_4 is preferably R_4'; more preferably R_4'';
R_5 is preferably R_5', more preferably hydrogen;
R_6 is preferably R_6', more preferably R_6'';
m is more preferably m';
R_7 is preferably R_7'; more preferably R_7'';
R_8 is preferably R_8'; more preferably R_8'';
R_9 is preferably R_9'; more preferably R_9'';
A is preferably A_1; more preferably A_1';
R_{12} is preferably R_{12}';
Z_1 is preferably Z_2;
R_{13} is preferably R_{13}';
R_{15} is preferably methyl;

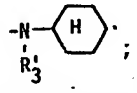
Preferably the floating sulpho group on the naphthyl rings is in the 3-position.

R_2 and/or R_4 when an aliphatic amine are or is preferably mono(C_{1-4}alkyl)amino; di-(C_{1-2}alkyl)amino, monohydroxyC_{1-4}alkylamino, more preferably $-N(C_2H_4OH)_2$ or $-NHC_2H_4OH$.

R_2 and/or R_4 when an aromatic amine are or is preferably



R_2 and/or R_4 when a cycloaliphatic amine are or is preferably



R_7, R_8 and/or R_9 when a substituted alkyl are or is hydroxyC_{2-3}alkyl, phenyl C_{1-3}alkyl, 2-cyanoethyl or 2-chloroethyl;

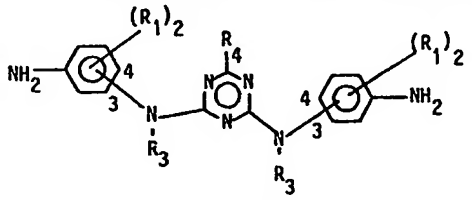
R_9 when alkyl is preferably methyl, ethyl or propyl; more preferably methyl or ethyl;

R_9 when a substituted alkyl is preferably cyanoethyl, hydroxyethyl, chloroethyl or benzyl, more preferably benzyl.

A when an alkylene group is preferably C_{1-8}alkylene, uninterrupted or interrupted by one $-NC_{1-4}$alkyl group (preferably $-N(CH_3)-$, more preferably uninterrupted C_{1-4}alkylene.

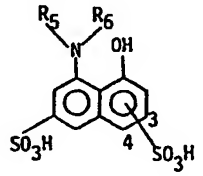
R_{13}, when $-NH_2$-substituted alkyl, is preferably $-C_2H_4NH_2$.

Compounds of formula I can be prepared by reacting one mole of the tetrazotised compound of the formula X



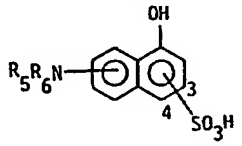
(X)

with 2 moles of a coupling component of formula XI



(XI)

or with 2 moles of a coupling component of formula XII



(XII)

or 1 mole of the coupling component of formula XI and 1 mole of the coupling component of formula XII.

Compounds of formula X, XI and XII are known or can be prepared from known compounds by known methods.

The SO_3H groups can be converted to the salt form by known methods.

Coupling to form compounds of formula I can be carried out according to known methods. Advantageously, coupling is carried out in aqueous (acid, neutral or alkali) medium at a temperature from −10°C to room temperature, if necessary in the presence of a coupling accelerator such as pyridine or urea. Alternatively, coupling may be effected in a mixture of solvents, for example water and an organic solvent.

Metallisation of compounds of formula I can be achieved by known methods.

The azo compounds of formula I in 1:1 metal complex form may be prepared by metallising compounds of formula I in metal-free form with a metal selected from copper, cobalt, iron, nickel, manganese, chromium and zinc.

The azo compounds of formula I in 1:2 metal complex form may be prepared by metallising compounds of formula I in metal-free form with a metal selected from chromium, nickel, cobalt and iron.

A further method for the preparation of an azo compound of formula I in 1:2 metal complex form comprises reacting an azo compound of formula I in metal-free form with an azo compound 1:1 metal complex when the metal is chromium, nickel, cobalt or iron.

The metallisation process to form a 1:1 metal complex is advantageously carried out by treating 1 mole of azo compound with a metallising agent containing 1 equivalent of metal.

Metallisation is carried out advantageously in aqueous medium or a mixture of water and a water-miscible organic solvent, for example acetone, lower alkyl alcohols, dimethylformamide, formamide, glycols or acetic acid at a pH range from 1.0 to 8.0, preferabnly pH 2 to 7. The metallisation process may be carried out at a temperature from room temperature to the boiling point of the reaction medium.

Alternatively, metallisation may be effected in a wholly organic medium (for example dimethylformamide). Advantageously, for instance, cobaltisation may be carried out in the presence of an inorganic nitrite such as lithium, sodium, ammonium or potassium nitrite in the ratio of 2 to 6 moles of nitrite per gram atom of cobalt.

Suitable cobalt-yielding compounds are, for example, cobalt (II) or Co (III) sulphate, acetate, formate or chloride.

Copper-yielding compounds are, for example cupric sulphate, cupric formate, cupric acetate and cupric chloride.

The nickel-yielding compounds are Ni (II) or Ni (III) compounds, such as nickel formate, nickel acetate and nickel sulphate.

Preferred manganese-yielding compounds are Mn (II) compounds in iron-yielding compounds are Fe (II) or Fe (III) compounds. Examples of these and zinc-yielding compounds are manganese, iron and zinc formate, acetate and sulphate.

Preferred chromium-yielding compounds are Cr (II) and Cr (III) formate, acetate and sulphate.

In the compounds of formula I the anions $A^{\ominus}$ can be any non-chromophoric anions such as those conventional in basic dyestuff chemistry. Suitable anions include chloride, bromide, sulphate, bisulphate, methylsuphate, aminosulphonate, perchlorate, benzenesulphonate, oxalate, maleate, acetate, propionate, lactate, succinate, tartrate, malate, methanesulphonate and benzoate, as well as complex anions, for example, zinc chloride double salts and anions of boric acid, citric acid, glycollic acid, diglycollic acid and adipic acid or addition products of orthoboric acid with polyalcohols with at least one *cis* diol group present. These anions can be exhanged for each other by ion exchange resins or by reaction with acids or salts (for example via the hydroxide or bicarbonate or according to German Offenlegungsschrift 2,001,748 or 2,001,816.

The azo compounds in quaternised and/or salt form are useful as dyes.

The azo compounds of formula I in quaternised and/or salt form are suitably worked up into solid or liquid preparations, for example by granulation or by dissolving in a suitable solvent. The compounds of formula I in quaternised form and/or salt form are suitable for dyeing, padding or printing on fibres, threads or textile materials, particularly natural or regenerated cellulose materials for example cotton, or synthetic polyamides or synthetic polyesters in which the acid groups have been modified. Such polyamides are described in Belgian Patent 706,104 and such synthetic polyesters are described in US Patent 3,379,723.

The dyes of formula I may also be applied to bast fibres such as hemp, flax, sisal, jute, coir or straw.

The dyes of formula I are also used for dyeing, padding or printing fibres, threads or textiles produced therefrom which consists of or contain homo- or mixed polymers of acrylonitrile or of 1,1-dicyanoethylene.

The textile material is dyed, printed or pad-dyed in accordance with known methods. Acid modified-polyamide is dyed particularly advantageously in an aqueous, neutral or acid medium, at temperature of 60°C to boiling point or at temperatures above 100°C under pressure.

The textile material may also be dyed by the compounds of formula I in organic solvents, e.g. in accordance with the directions given in German Offenlegungschrift 2,437,549.

Cellulose material is mainly dyed by the exhaust process, i.e. from a long or short bath, at room temperature to boiling optionally under pressure, whereby the ratio of the bath is from 1:1 to 1:100 and preferably from 1:20 to 1:50. If dyeing is effected from a short bath, then the liquor ratio is 1:5 to 1:15. The pH of the dye bath varies between 3 and 10 (for short and long dyebaths). Dyeing preferably takes place in the presence of electrolytes.

Printing may be effected by impregnation with a printing paste produced by known methods.

The dyes of formula I are also suitable for dyeing or printing paper, e.g. for the production of bulk-dyed, sized and unsized paper. The dyestuffs may similarly be used for dyeing paper by the dipping process. The dyeing of paper is effected by known methods.

The dyes of formula I are also suitable for dyeing or printing leather by known methods.

Dyeings with good fastness are obtained on both paper and leather.

Dyeings made with the dyes of formula I on leather have good light fastness properties, good diffusion properties with PVC, good water-, wash and sweat-fastness properties, good fastness to dry cleaning, good fastness to drops of water and good fastness to hard water.

Dyeings prepared with dyes of formula I on paper produce a substantially clear spent liquor which is important for environmental reasons. The dyes of formula I have good build-up properties and are of high substantivity, do not run once applied to paper and are not pH sensitive. Dyeings produced with dyes of formula I have good light fastness and the nuance on exposure for a long time to light fades tone-in-tone. The dyes of formula I have good wet-fastness properties not only for water but also for milk, soap, water, sodium chloride solution, fruit juice and sweetened mineral water. Further dyeings made with dyes of formula I are fast for alcoholic beverages due to a good alcohol fastness. Further the dyes of formula I have good nuance stability.

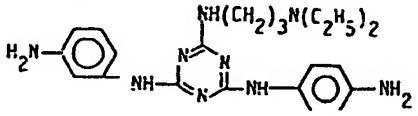
The dyes of formula I may be converted into dyeing preparations. Processing into stable liquid or solid dyeing preparations may take place in a generally known manner, advantageously by grinding or granulating or by dissolving in suitable solvents, optionally adding an assistant, e.g. a stabiliser or dissolving intermediary such as urea. Such preparations may be obtained, for example, as described in French Patent Specifications 1,572,030 and 1,581,900 or in accordance with German DOS 2,001,748 and 2,001,816.

Liquid preparations of the compounds of formula I preferably comprise 10 to 30 % by weight of a compound of formula I up to 30 % of a solubilising agent such as urea, lactic acid or acetic acid and the rest of the composition being water. Solid preparations preferably comprise 20 to 80 % dyestuff, 20 to 80 % solubilising agent such as urea or Na_2SO_4 and 2 to 5 % water.

The invention will now be illustrated by the following Examples in which all parts and percentages are by weight and all temperatures are in °C unless indicated to the contrary.

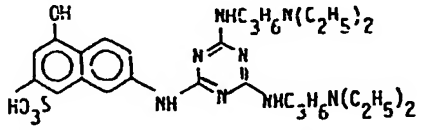
Example 1

4.2 of the diamine of formula 1a



(1a)

are tetrazotised by known methods and coupled in aqueous medium at a pH of 3.5 and at a temperature of 10-20° to 11.5 g to the compound of formula 1b



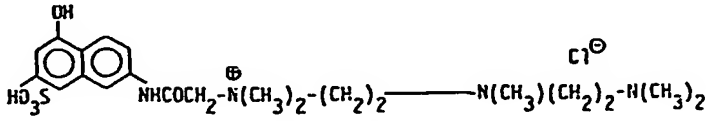
(1b)

The resulting dyestuff dyes paper a scarlet tone and the dyeings so produced have good wet and light fastness properties. The resulting dyestuff has a high substantivity.

The compound of formula 1a can be prepared by reacting 2 moles of an aminonitrobenzene with cyanuric acid in aqueous medium to form the corresponding dinitro compound in which the chloroatom is replaced by reacting with $NH_2-C_3H_6N(C_2H_5)_2$ at 70 to 90° in aqueous or organic solution followed by reducing the nitro groups by the Béchamps reduction.

Example 2

Instead of using the compound of formula 1b in the process of Example 1, 9.0 g of the compound of formula 2a

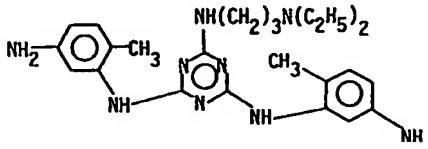


(2a)

are used. The resulting compound dyes paper a red tone and has good fastness properties.

Example 3

Instead of using the compound of formula Ia in the method of Example 1, 4.3 g of a compound of formula 3a

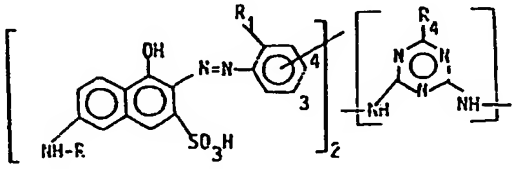


can be used instead.

The resulting brilliant scarlet dye dyes paper a red colour and the dyeings so produced have good properties.

Examples 4 to 64

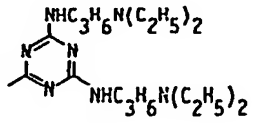
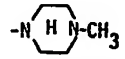
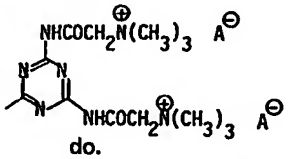
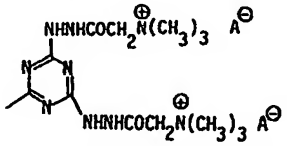
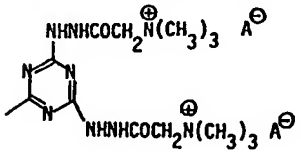
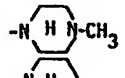
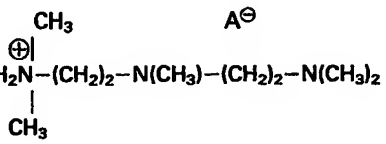
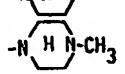
Compounds of formula

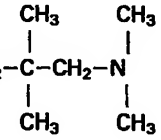
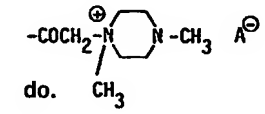
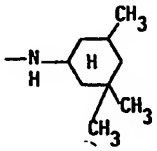
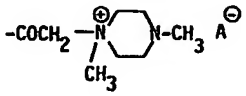
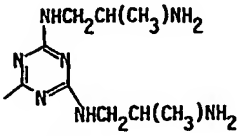
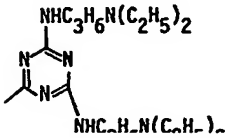


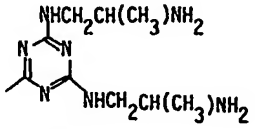
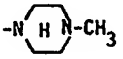
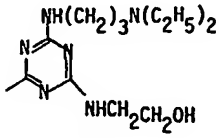
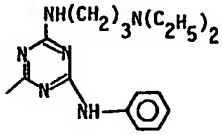
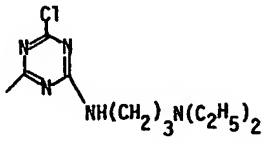
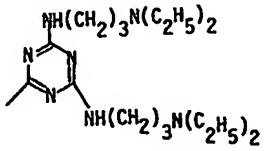
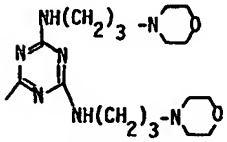
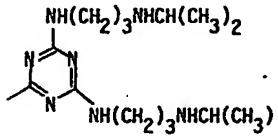
in which R and R_1 are given in Table 1 below and the position of the floating bond from the triazinyl group in the phenyl rings is given in column s, can be made by a method analogous to that of Example 1.

Dyeings made on paper with the compounds of Examples 53 and 56 are bordeaux red nuance; those made with the compounds of Examples 4, 5, 6 to 16, 18, 20, 21, 45 to 48, 50, 52 and 58 to 64 of a scarlet nuance; those made with the compounds of Examples 17, 19, 22 to 44 are a scarlet red nuance; those made with compounds of Examples 49, 54 and 57 are an orange nuance and those made with compounds of Examples 52 and 55 are blueish red nuance.

TABLE 1

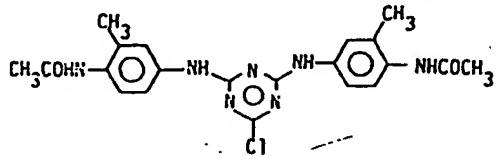
Ex. No.	S	R	R_4	R_1
4	3,3			H
5	3,3	do.		H
6	3,3	do.	$-NHCH_2CH_2OH$	H
7	3,3	do.	$-NHCH_2CH_2NH_2$	H
8	3,3	do.	$-NH(CH_2)_2NH(CH_2)_2NH_2$	H
9	3,3	do.	$-NH_2$	H
10	3,3	do.	$-OH$	H
11	3,3	do.		H
12	3,3	do.	$-NHC_3H_6N(CH_3)_2$	H
13	3,3		$-NHC_3H_6N(C_2H_5)_2$	H
14	3,3	do.	$-NH_2$	H
15	3,3			H
16	3,3		$-NHC_3H_6(C_2H_5)_2$	H
17	3,3	$-COCH_2\overset{\oplus}{N}(CH_3)_2-(CH_2)_3-N(CH_3)_2\,A^{\ominus}$	do.	H
18	3,3	do.		H
19	3,3	do.		H
20	3,3	do.		H
21	3,3	do.	$-NHC_3H_6OCH_3$	H
22	3,3		do.	H
23	3,3	do.	$-NHCH_2CH_2NH_2$	H
24	3,3	do		H
25	3,3	do.		H
26	3,3	do.		H

27	3,3	do.	$-NHCH_2CH_2OH$	H	
28	3,3	$-COCH_2\overset{\oplus}{N}(CH_3)_2(CH_2)_2N(CH_3)-(CH_2)_2N(CH_3)_2$ $A^{\ominus}$	$-N(CH_2CH_2OH)_2$	H	
29	3,3	$-COCH_2\overset{\oplus}{N}(CH_3)_2(CH_2)_2N(CH_3)(CH_2)_2N(CH_3)_2$		H	
30	3,3	do.	$-NH(CH_2)_3OCH(CH_3)_2$	H	
31	3,3	do.	$-NH(CH_2)_2NH(CH_2)_2NH_2$	H	
32	3,3	do.	$-NHCH_2CHOHCH_2NH_2$	H	
33	3,3	do.		H	
34	3,3	$-COCH_2\overset{\oplus}{N}(CH_3)_2(CH_2)_4N(CH_3)_2\,A^{\ominus}$	$-NHC_3H_6N(C_2H_5)_2$	H	
35	3,3	do.		H	
36	3,3		$-NHC_3H_6N(C_2H_5)_2$	H	
37	3,3	do.		H	
38	3,3	do.		H	
39	3,3	do.	$-NHCH_2CH_2OH$	H	
40	3,3	do.	$-NHCH_2CH_2NH_2$	H	
41	3,3	do.		H	
42	3,3		$-NHCH_2CH_2NHCH_2CH_2OH$	H	
43	3,3	do.	$-NHCH_2CH_2OCH_2CH_2OH$	H	
44	3,3	do.	$-NH_2$	H	
45	3,3	do.		H	
46	3,3		$-NHCH_2CH(CH_3)NH_2$	H	
47	3,3	do.	$-NHCH_2CH_2OH$	H	
48	3,3	do.		H	
49	3,3	do.	$-NH(CH_2)_3N(CH_3)_2$	SO_3H	
50	3,3	do.	$-NH(CH_2)_3N(C_2H_5)_2$	do.	
51	3,3	do.		do.	
52	3,3		do.	$-CH_3$	

53	3,3	do.	do.	$-OCH_3$	
54	3,3	do.	do.	$-SO_3H$	
55	3,3			CH_3	
56	3,3	do.	do.	$-OCH_3$	
57	3,3	do.	do.	$-SO_3H$	
58	3,3		do.	H	
59	3,3		do.	H	
60	3,3		do.	H	
61	3,3		Cl	H	
62	3,3		$-NH(CH_2)_3N(C_2H_5)_2$	H	
63	3,3		$-NH(CH_2)_3N(C_2H_5)_2$	H	
64	3,3		do.	H	

Example 65

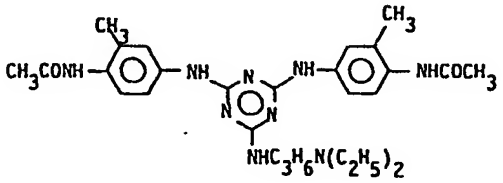
9.2 Parts of cyanuric chloride are suspended in 100 parts water and 100 parts ice and the product is then reacted with 16.4 parts of 4-amino-2-methylacetanilide. The temperature is allowed to rise to 25° whilst at the same time maintaining the pH between 5 and 6 by the addition of sodium carbonate. After there is no further visible reaction, the reaction mass is heated to 60° whilst at the time maintaining the pH constant at 5 to 6 and stirring for 3 hours at this temperature. At the end of this time the condensation is finished and the compound of formula 65a



(65a)

is formed.

Without isolating, the suspension is reacted with 25 parts of N,N-diethylaminopropylamine and stirred for 10 hours at 92°. After this period is over this condensation step is finished. The suspension is filtered hot and the residue is washed with water. 27 Parts of the compound of formula 65b



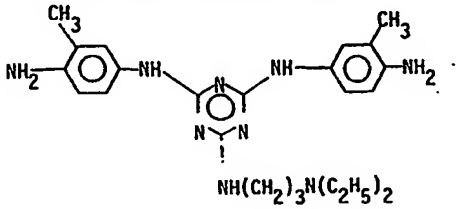
(65b)

is formed (which is grey in colour).

27 Parts of the residue are suspended in 200 parts of water and reacted with 50 parts of 30 % hydrochloric acid solution.

The mixture is then heated to 95°C. After about one hour saponification has finished. The solution is then clear filtered after cooling.

The solution contains 20 parts of the compound of formula 65c



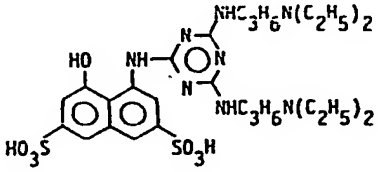
(65c)

which can be used as a tetraazo component.

Instead of using 4-amino-2-methylacetanilide an equivalent amount of one of the following can be used:

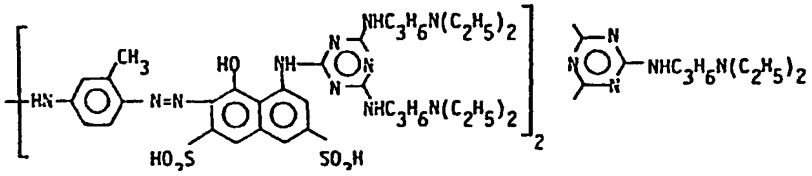
4-amino-2-methoxyacetanilide
4-amino-2-chloroacetanilide
4-amino-2,5-dimethylacetanilide
4-amino-2-methoxy-5-methylacetanilide
4-amino-2,5-dimethoxyacetanilide
4-amino-acetanilide
3-aminoacetanilide

60 Parts by volume of an aqueous, hydrochloric acid solution (containing 3 parts of the compound of formula 65c) is brought to 0° and to which 14 parts by volume of a 1 N sodium nitrite solution are dropwise added. A yellow tetraazo solution is formed to which 10 parts of the compound of formula 65d



(65d)

dissolved in 70 parts of water are added. The pH is regulated between 6 and 8 by the addition of sodium carbonate and coupling occurs. A blue dyestuff solution results. After coupling 40 parts of sodium chloride and 10 parts of 30 % aqueous sodium hydroxide are added. The dyestuff precipitates so filtered and after drying, 26 parts of the compound of formula 65e



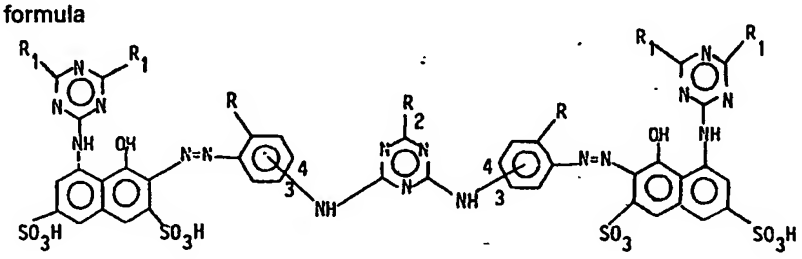
(65e)

are formed.

In acid addition salt form this compound dyes paper neutral blue tone. The back water is colourless and the dyed paper obtains very good wet fastnesses.

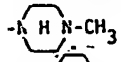
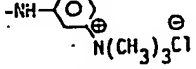
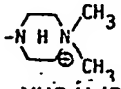
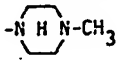
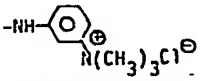
Examples 66 to 88

Compounds of the formula



in which R, R_1 and R_2 are defined in Table 2 below. The position s of the amino group on the phenyl groups, are formed by a method analogous to that of Example 65 from appropriate reactants.

TABLE 2

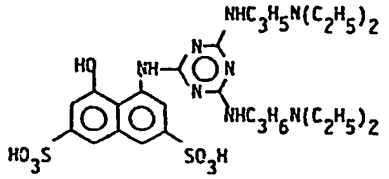
Ex. No.	S	R_1	R_2	R_4
66	4,4	CH_3	$-NHC_3H_6N(C_2H_5)_2$	$-NHC_3H_6N(CH_3)_2$
67	4,4	CH_3	do.	$-NHC_2H_4NH_2$
68	4,4	CH_3	do.	
69	4,4	CH_3	do.	
70	4,4	CH_3	do.	
71	4,4	CH_3	$-NHC_3H_6N(CH_3)_2$	$-NHC_3H_6(CH_3)_2$
72	4,4	OCH_3	$-NHC_3H_6N(C_2H_5)_2$	$-NHC_3H_6N(C_2H_5)_2$
73	4,4	OCH_3	do.	
74	4,4	OCH_3	do.	
75	4,4	H	$-NHC_3H_6N(CH_3)_2$	$-NHC_3H_6N(CH_3)_2$
76	4,4	H	$-NHC_3H_6N(C_2H_5)_2$	$-NHC_3H_6N(C_2H_5)_2$
77	4,4	H	$-NHNHCOCH_2\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{Cl}$	$-NHC_3H_6N(C_2H_5)_2$
78	4,4	CH_3	do.	do.
79	4,4	OCH_3	do.	do.
80	4,4	H	$-NHC_3H_6N(C_2H_5)_2$	$-NHNHCOCH_2\overset{\oplus}{N}(CH_3)_3\ \overset{\ominus}{Cl}$
81	4,4	CH_3	do.	do.
82	4,4	OCH_3	do.	do.
83	4,4	Cl	do.	$-NHC_3H_6N(C_2H_5)_2$
84	4,4	Cl	$-NHC_3H_6N(C_2H_5)_2$	$-NHC_3H_6N(CH_3)_2$
85	3,3	H	do.	$-NHC_3H_6N(C_2H_5)_2$
86	3,3	Cl	do.	do.
87	3,3	OCH_3	do.	do.
88	3,3	CH_3	do.	do.

The nuances of the above Examples 66 to 88 are given below:

Nuance	*Example Nos.*
neutral blue	66 to 71, 78, 81
greenish blue	72 to 74, 79, 82
reddish blue	75 to 77, 80
blueish red	83, 84
bordeaux	85
rubin red	86
violet	87
reddish violet	88

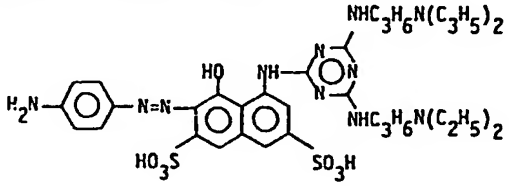
Example 89

4.6 Parts of 4-aminoacetanilide are reacted with 8 parts of 30 % hydrochloric acid in 100 parts of water and 100 parts of ice. The product is diazotised with aqueous sodium nitrite solution. To the resulting solution 26 parts of the compound of formula 89a



(89a)

are added, the pH being regulated to 7.5 with sodium carbonate. A violet dyestuff is produced. After filtering and washing the residue is stirred in 300 parts of water and is dissolved with 30 parts of volume concentrated hydrochloric acid. This solution is then warmed to 90 to 95°C and is stirred for 3 hours at this temperature. At the end of the 3 hours saponification has finished and 380 parts by volume of a blue dyestuff solution result containing 22.4 parts of the compound of formula 89b



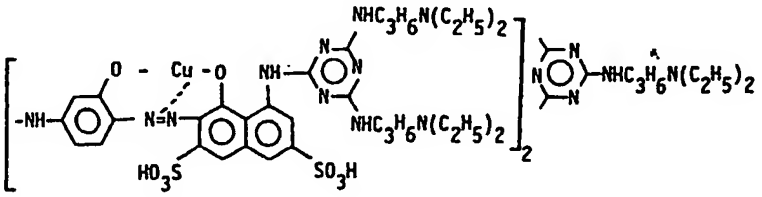
(89b)

To 135 parts by volume of this solution 32 parts by volume of a 4N sodium carbonate solution are added to bring the solution to a pH of 6. 0.92 Parts of cyanuric chloride dissolved in 10 parts by volume acetone, are added and stirred for 30 minutes at room temperature. The pH is held at 6 by the addition of a 4N sodium carbonate solution. Finally the solution is heated to 60° and the pH is held for a further 2 hours at 5 to 6. At the end of this 2 hour period, the condensation has ended. 2 Parts by volume of N,N-diethylaminopropylamine are then added.

The temperature is raised to 90° and the acetone is distilled off. The reaction mass is then held at 90 to 95° for 4 hours and at the end of this 4 hour period condensation has finished. After cooling to room temperature, 50 parts of NaCl are added. The dyestuff precipitates out and is then filtered. After drying, 21 parts of a dark powder result containing 6.3 parts of the compound of Example 77. The aminoazo dyestuff of formula 89b can be prepared directly according to DOS 2,555,515 using p-phenylenediamine instead of 4-aminoacetanilide.

Example 90

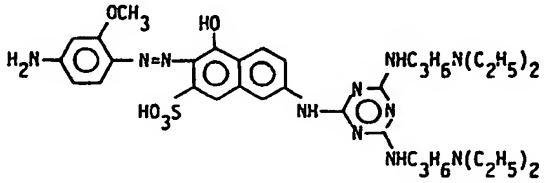
44 Parts of the dyestuff of Example 72 are stirred in 500 parts of water and the pH is brought to 6 with glacial acetic acid, at which pH the dyestuff dissolves to form a solution. 14.7 Parts of $CuSO_4$ pentahydrate dissolved in 100 parts of a 25 % ammonia solution, are added. The solution is heated to 93° and stirred for 8 hours. At the end of this period copperisation has almost been completed. The mass is stirred when cold and reacted with 75 parts by volume of a 30 % NaOH solution. The majority of dyestuff present precipitates. The residue is then filtered and dried under mild conditions. A dyestuff of formula 90a



results. When in acid addition salt form this dyes paper a violet-blue tone. The backwater of such dyeings is practically colourless and the dyed paper shows very good wet fastness properties. Good light fastness properties have also been found.

Example 91

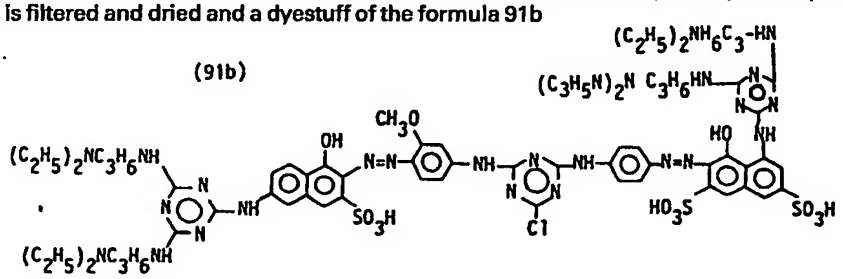
7.7 Parts of the compound of formula 98b (described in Example 89) are dissolved in 300 parts of water at a pH value of 6 and are then cooled to 5°. 1.9 Parts of cyanuric chloride, dissolved in 10 parts of acetone, are added dropwise so that the temperature does not rise over 5°. The mass is stirred at this temperature for 3 hours and the pH is then brought to 5 to 6 by adding sodium acetate. After checking with the aid of a thin layer chromatograph that no aminoazo dyestuff is present, 7.2 parts of a compound of formula 91a



(91a)

are added and the temperature is slowly raised to 60°, maintaining the pH at 5 to 6 by the further addition of sodium acetate. The mass is then allowed to cool to room temperature and is reacted with 50 parts of sodium chloride. 20 Parts of a 30 % NaOH is then added and the majority of the dyestuff present precipitates out. The residue is filtered and dried and a dyestuff of the formula 91b

(91b)

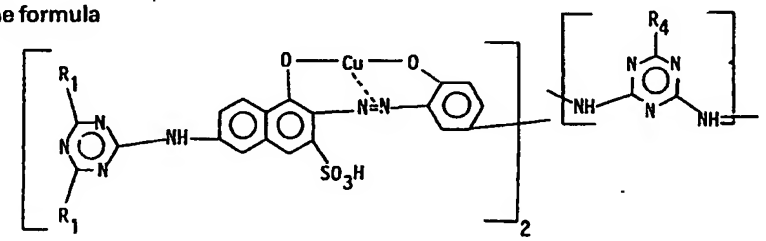


results. When in acid addition salt form the dyestuff of formula 91b dyes paper a violet-blue nuance. The backwater is colourless and the wet fastness properties of the dyed paper are very good.

The dyestuff of formula 91b can be stirred in the presence of N,N-diethylaminopropylamine at 95 to 98°C until exchange of the chlorine atoms for the amine occurs. The resulting dyestuff dyes paper a blue tone with good wet fastness and light fastness properties.

Examples 92 to 95

Compounds of the formula



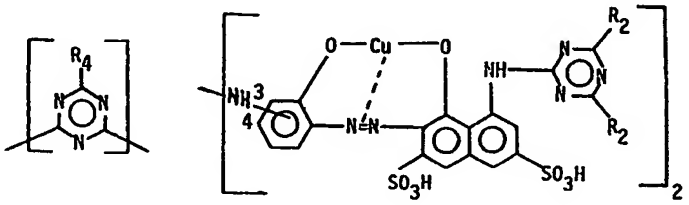
in which the symbols R_1 and R_4 are defined in can be made by a method analogous to that of Example 89 from appropriate starting materials

TABLE 3

Ex. No.	R_2	R_4	nuance
92	$-NH(CH_2)_3-N(C_2H_5)_2$	$-NH(CH_2)_3N(C_2H_5)_2$	red-orange
93	do.	$-NHCH_2CH_2OH$	do.
94	do.		do.
95	$-NHCH_2CH(CH_3)NH_2$	$-NH(CH_2)_3N(C_2H_5)_2$	do.

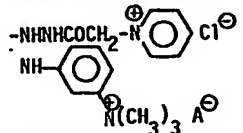
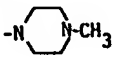
Examples 96 to 99

Compounds of the formula



in which R_2, R_4 and the position s of the —NH group on the phenyl ring are given in Table 4 below, can be prepared from appropriate reactants by a method analogous to that of Example 90.

TABLE 4

Example No.	R_3	R_4	S	nuance
96	$-NHC_3H_6N(C_2H_5)_2$	$-NHC_3H_6N(C_2H_5)_3$	3	violet
97		$-NHC_3H_6N(CH_3)_2$	4	violet-blue
98		do.	3	violet-blue
99	$-NHC_3H_6N(CH_3)_2$		3	violet

Dyeing Example A

70 Parts of chemically bleached sulphite cellulose (of pinewood) and 30 parts of chemically bleached sulphite cellulose (of birchwood) are ground in a Hollander in 2000 parts of water. 0.2 Parts of the dyestuff described in Example 1 are sprinkled into this pulp. After mixing for 20 minutes, paper is produced from this pulp. The absorbent paper obtained in this way is dyed scarlet. The waste water is practically colourless.

Dyeing Example B

0.5 Parts of the dyestuff of Example 1 are dissolved in 100 parts of hot water and cooled to room temperature. This solution is added to 10 parts of chemically bleached sulphite cellulose which have been ground in a Hollander with 2000 parts of water. After thorough mixing for 15 minutes, sizing takes place. Paper which is produced from this matter has a scarlet shade of average intensity, with good wet fastness properties.

Dyeing Example C

An absorbent length of unsized paper is drawn through a dyestuff solution of the following composition at 40 to 50°. 0.5 Parts of the dyestuff of Example 1, 0.5 parts of starch and 99.0 parts of water. The excess dyestuff solution is squeezed out through two rollers. The dried length of paper is dyed scarlet with good fastness.

Dyeing Example D

2 Parts of the dyestuff according to Example 1 are dissolved at 40° in 4000 parts of softened water. 100 Parts of premoistened cotton fabric are entered into the bath, which is heated for 30 minutes to boiling temperature. The bath is kept at boiling temperature for 1 hour, and the water which evaporates is replaced from time to time. The dyeing is then removed from the liquor, rinsed with water and dried. The dyestuff is adsorbed practically quantitatively on the fibres; the dye bath is practically colourless. A reddish-yellow dyeings is obtained with good light fastness and good wet fastness.

In Dyeing Examples A to D an appropriate amount of any one of Dyestuffs 2 to 88 in liquid or granulate preparation form may be used instead of the amount of the dyestuff of Example 1 to produce good dyeings with good fastness properties.

Application Example E

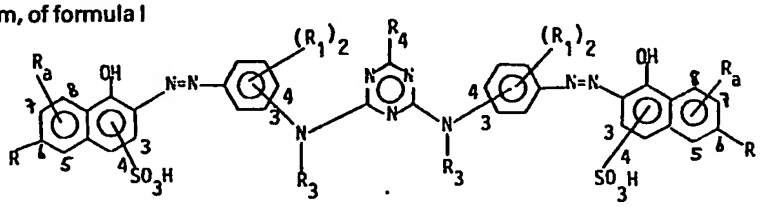
100 Parts freshly tanned and neutralised chrome leather are agitated for 30 minutes in a vessel with a dyebath of 250 parts water at 55°C and 0.5 parts of the dyestuff of Example 1 in acid addition salt form, and then treated in the same bath for 30 minutes with 2 parts of an anionic fatty liquor based on sulphonated train oil. The leather is then dried and prepared in the normal way, giving a leather evenly dyed in a black tone.

Other low affinity vegetable-tanned leathers can similarly be dyed by known methods.

In the above Dyeing Examples A to E instead of using the dyestuff of Example 1 an appropriate amount of any one of Examples 2 to 99 may be used.

CLAIMS

1. A compound in metal-free, 1:1 metal complex or 1:2 metal complex form and in free acid or acid addition salt form, of formula I



where each R independently is hydrogen, SO_3H or NR_5R_6 and each R_a independently is hydrogen or NR_5R_6 provided that R and R_a on the same naphthyl group are not both the same; that one of R and R_a on the same naphthyl group is $-NR_5R_6$; and when R is SO_3H R_a on the same naphthyl ring is in the 8-position.

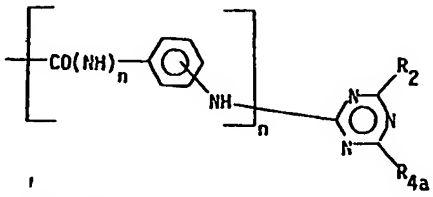
each R_1 independently is hydrogen, halogen, OH, C_{1-4}alkyl, C_{1-4}alkoxy or SO_3H;

each R_3 independently is hydrogen or C_{1-4}alkyl;

R_4 is halogen, OH, C_{1-4}alkoxy, phenyl, $-NH_2$ an aliphatic, cycloaliphatic, aromatic or heterocyclic amine which may contain 1 to 3 heteroatoms; or a hydrazine group; in which the N-atom of the amine or hydrazine is attached to the C-atom of the triazinyl group and the amine or hydrazine group can bear protonatable basic groups and/or quaternary N-atoms;

each R_5 independently is hydrogen or C_{1-4}alkyl;

each R_6 independently is a group of the formula a) or b)



a)

(b)

where each n independently is 0 or 1 and each m independently is 1, 2, 3 or 4;

R_2 is an aliphatic, cycloaliphatic, aromatic or heterocyclic amine or hydrazine group in which the N-atom is attached to the C-atom of the triazinyl group and the amine or hydrazine group can bear protonatable basic groups and/or quaternary N-atoms;

R_{4a} has a significance of R_4 independent of R_4

Ka is $N(R_7)_2$; $-\overset{\oplus}{N}(R_8)_2R_9\ A^{\ominus}$; $-\overset{\oplus}{N}(R_8)_2-A-N(R_7)_2\ A^{\ominus}$ or $\overset{\oplus}{N}(R_8)_2-A-N(R_8)_2R_9\ 2\ A^{\ominus}$

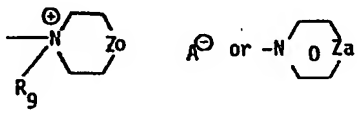
where each R_7 independently is hydrogen; unsubstituted C_{1-6}alkyl; C_{2-6}alkyl substituted by one of OH, CN and halogen; phenyl C_{1-3}alkyl, the phenyl group of which is unsubstituted or substituted by 1 to 3 substituents selected from halogen, C_{1-4}alkyl and C_{1-4}alkoxy; or C_{5-6}cycloalkyl unsubstituted or substituted by 1 to 3 (C_{1-4})alkyl groups or

both R_7's together with the N-atom to which they are attached form a five- or six-membered saturated heterocyclic ring containing one to three heteroatoms;

each R_8 independently has a non-cyclic or cyclic significance of R_7 except hydrogen; and

each R_9 independently is C_{1-4}alkyl unsubstituted or substituted by one of phenyl, $-CONH_2$ and unsubstituted cyclohexyl or C_{2-4}alkyl substituted by one of OH, halogen and CN; or C_{3-8}alkenyl or $-(CH_2)_2-CO(C_{1-4}$alkyl);

or both R_8's and R_9's together with the N-atom to which they are attached form a group of the formula



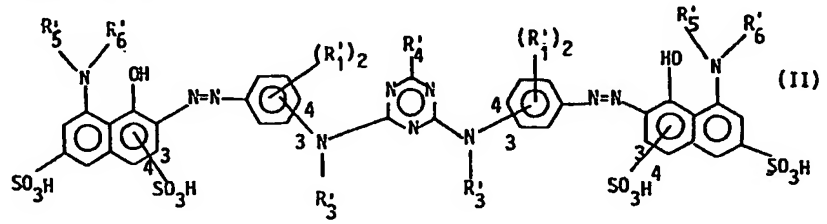
where Z_o is $-O-$, a direct bond, $-CH_2-$; $-NH-$, $-NC_{1-4}$alkyl;

$-\overset{\oplus}{N}(C_{1-4}alkyl)_2\ A^{\ominus}$; $-SO_2-$, $-SO-$, $-S-$; or $-N-(CH_2)_{2-3}-NH_2$;

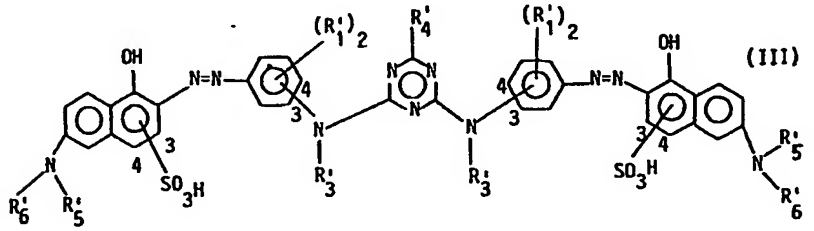
Za is $-CH_2-$ or a direct bond
or a heterocyclic amine, unsubstituted or substituted by 1 to 3 C_{1-4}alkyl groups;
each A independently is C_{1-12}alkylene uninterrupted or interrupted by 1 to 3 heteroatoms; or unsubstituted C_{3-8}alkenylene; and
$A^{\ominus}$ is a non-chromophoric anion;
with the provisos:-

i) that the sum of cationic and protonable basic groups exceeds the sum of sulpho and anionic groups by at least one; and
ii) that the sulpho groups on the naphthyl groups are in the 3- or 4-position (shown);
iii) that the $-NR_3$ groups on the phenyl rings are in the 3- or 4-position (shown)
iv) that when both R's are $-NR_5R_6$, both R_6 s are a group of formula a) and both n s are zero then both $-NR_3$ groups are in the 3-position (shown) on the phenyl rings.

2. A compound according to Claim 1 in metal-free, 1:1 or 1:2 metal complex form or in free acid or acid addition salt form of formulae II or III

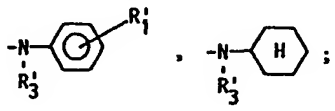


(II)

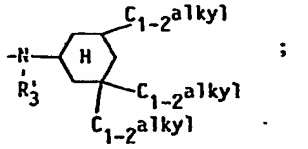


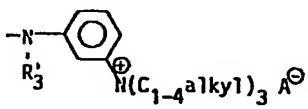
(III)

in which
R_1' is hydrogen, Cl, Br, CH_3, OCH_3 or SO_3H
R_3' is hydrogen or CH_3;
R_4' is Cl, Br, $-NH_2$, $-CH_3$, $-OH$, phenyl, OCH_3,



mono(C_{1-4}alkyl)amino, di(C_{1-4}alkyl)amino, monohydroxy C_{2-4}alkylamino, bis-(hydroxyC_{2-4}alkyl)amino;

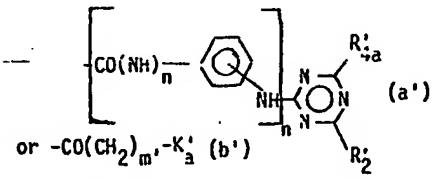




or R_2' defined below;

R_5' is hydrogen, methyl or ethyl;

R_6 is



(a')

or $-CO(CH_2)_{m'}-K_a'$ (b')

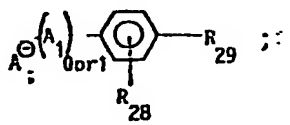
where m' is 1, 2 or 3;

R_{4a}' has a significance of R_4' independent of R_4'

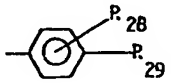
R_2' is $-N(R_{20}')-$;

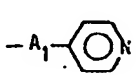
R_5'

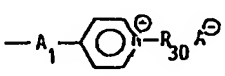
where R_{20}' is C_{1-12}alkyl, unsubstituted or substituted by one $-OH$ and uninterrupted or interrupted by one to three groups selected from $-N(R_7)-$ and $-\overset{\oplus}{N}(R_8)_2\,A^{\ominus}$; $-NHCOCH_2-Z$; $-CH_2CONH-A_1-Z$; A_1-Z;

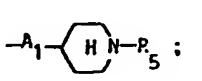


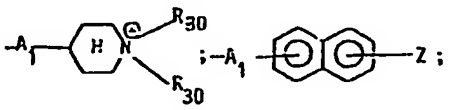
or

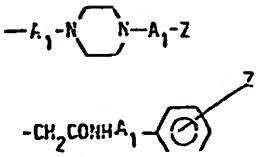


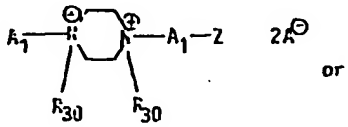












or

where

A_1 is C_{1-8}alkylene uninterrupted or interrupted by $-O-$, $-S-$, or

$-NR_5'$

or a C_{3-8} alkenylene group;

Z is $-N(R_7)_2$; $-\overset{\oplus}{N}(R_8)_2R_9\,A^{\ominus}$; $-A_1-Z_1$; $-CO-NH-A_1-Z_1$; $-NH-CO-A_1-Z_1$; $-CO-A_1-Z_1$; $-SO_2-NH-A_1-Z_1$ or $-NHNHCOCH_2-Z_1$

R_{28} is halogen, $-OH$, $-NO_2$, C_{1-4}alkyl or C_{1-4}alkoxy;

R_{29} is a group $-N(R_7')_2$ or $-\overset{\oplus}{N}(R_8')_2R_9'\,A^{\ominus}$ or a group $-CO-A_2-Z_1$, $-NHCO-A_2-Z_1$, $-CONH-A_2-Z_1$, $-SO_2NH-A_2-Z_1$; $-A_2-Z_1$ or $-NHNHCOCH_2-Z_1$;

A_2 is C_{1-8}alkylene;

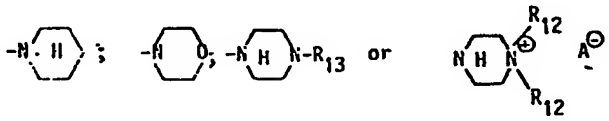
R_{30} is C_{1-4}alkyl;

Z_1 is $-N(R_7')_2$ or $-\overset{\oplus}{N}(R_8)_2R_9\,A^{\ominus}$

where

R_7', R_8' and R_9' are defined below; or

R_2' is a group of the formula



where

R_{12} is C_{1-4}alkyl;

R_{13} is hydrogen or C_{1-4}alkyl unsubstituted or substituted by $-NH_2$;

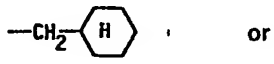
Ka is $N(R_7')_2$; $-\overset{\oplus}{N}(R_8')_2R_9'\ A^{\ominus}$; $-\overset{\oplus}{N}(R_8')_2-A-N(R_7')_2\ A^{\ominus}$ or $-\overset{\oplus}{N}(R_8')_2A-\overset{\oplus}{N}(R_8')_2R_9'\ 2A^{\ominus}$

R_7' is hydrogen, linear or branched C_{1-4}alkyl, linear hydroxyC_{2-3}alkyl, 2-cyanoethyl, 2-chloroethyl or phenyl (C_{1-3}alkyl), the phenyl group of which is unsubstituted or substituted by 1 to 3 substituents selected from Cl, CH_3 or OCH_3;

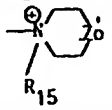
or both R_7 together with the N-atom to which they are attached form an unsubstituted morpholine, piperidine, pyrrolidine, piperazine or N-methylpiperazine group;

R_8' has a non-cyclic or a cyclic significance of R_7 other than hydrogen; and

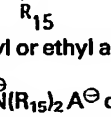
R_9' is methyl, ethyl, propyl, cyanoethyl, hydroxyethyl, chloroethyl, benzyl, $-CH_2-CH=CH_2$, $-CH_2-CO-CH_3$, $-CH_2CONH_2$ or



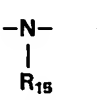
both R_8's and R_9' together with the N-atom to which they are attached form unsubstituted pyridine, picoline, lutidine or



or



where R_{15} is methyl or ethyl and Z' is $-CH_2-$, $-O-$, $-NH-$,



with the provisos

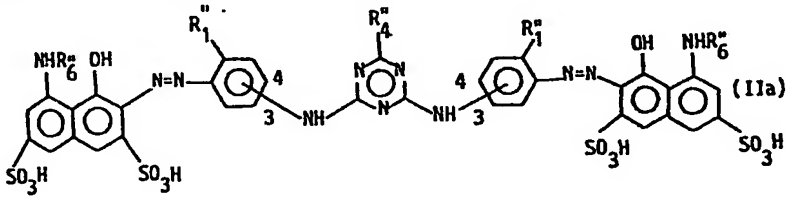
i) that in the compounds of formulae II and III the sum of cationic and protonatable basic groups exceeds the sum of sulpho groups and anionic groups by at least one; and

ii) that in the compounds of formulae II and III the floating sulpho groups on the naphthyl groups are in the 3- or 4-position (shown);

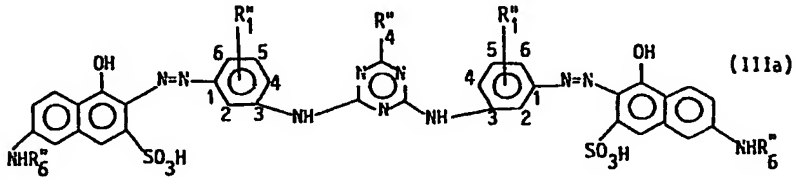
iii) that in the compounds of formula II and III the floating $-NR_3'$ groups are in the 3- or 4-position (shown); and

iv) that in the compounds of formula III when both R_8's are a group of formula a' and both n's are zero, then both $-NR_3'$ groups are in the 3-position on the phenyl groups and R_2' and R_{4a}' are not piperazine.

3. A compound according to Claim 1 in metal-free, 1:1 metal complex or 1:2 metal complex form or in free acid or acid addition salt form, of formula IIa or IIIa



(IIa)



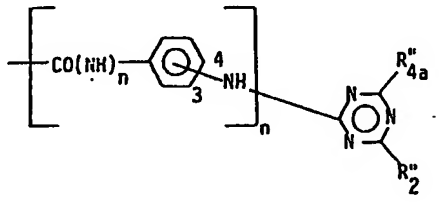
(IIIa)

in which

R_1'' is hydrogen, methyl, $-SO_3H$ or OCH_3;

R_4'' is Cl, NH_2, CH_3, OCH_3, OH, $-N(C_2H_4OH)_2$ $-NHC_2H_4OH$ or R_2'' (defined below);

R_6'' is a group of the formula



or is $-CO-(CH_2)_{m''}-K''_2$;

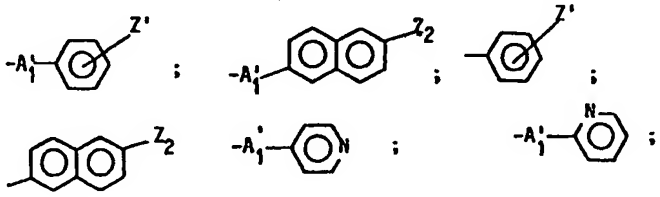
where

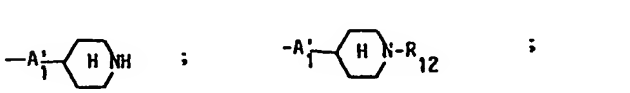
m'' is 1 or 2;

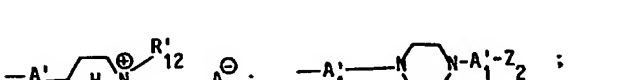
R''_{4a} has a significance of R''_4 independently of R''_4.

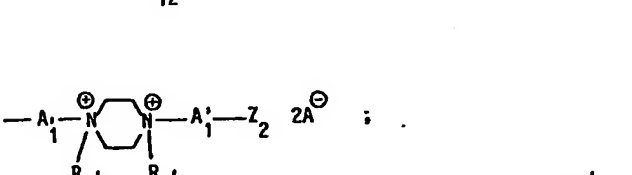
R''_2 is $-N(R'_5)-R''_{20}$;

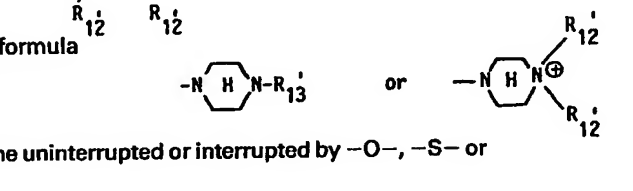
where R''_{20} is C_{1-12}alkyl, unsubstituted or substituted by one $-OH$ $-NR''_7R'_{12}$; $-(CH_2)_{2-3}-\overset{\oplus}{N}(R''_8)_2-(CH_2)_{2-3}-\overset{\oplus}{N}(R''_8)_2R'_{12}\,A^{\ominus}$; $-(CH_2)_{2-3}-N\,R''_7\,R'_{12}$; $-(CH_2)_{2-3}-\overset{\oplus}{N}(R''_8)_2\,R'_{12}\,A^{\ominus}$; $-NHCOCH_2-Z_2$; $-CH_2CONH-A'_1-Z_2$; $-A'_1-Z_2$;











or R''_2 is a group of the formula

where A'_1 is C_{1-8}alkylene uninterrupted or interrupted by $-O-$, $-S-$ or

$-N(R'_5)-$;

Z' is $-N(CH_3)_2$, $-\overset{\oplus}{N}(CH_3)_3\,A^{\ominus}$; $-CONH-A'_1-Z_2$; $-SO_2NH-A_1'-Z_2$; $-A_1-Z_2$; $-NHNHCOCH_2-Z_2$ or $CO-A_1'-Z_2$;

R'_{12} is methyl or ethyl;

R'_{13} is hydrogen or methyl or $-C_2H_4NH_2$;

Z_2 is a group $-N(R''_7)_2$ or $-\overset{\oplus}{N}(R''_8)_2R''_9\,A^{\ominus}$;

K''_a is a group of formula $-N(R''_7)_2$; $-\overset{\oplus}{N}(R''_8)_2-A_3-\overset{\oplus}{N}(R''_7)_2\,-\overset{\oplus}{N}(R''_8)_2-A_3-\overset{\oplus}{N}(R''_8)_2R''_9\,2\,A^{\ominus}$; $-\overset{\oplus}{N}(R''_8)_2R''_9\,A^{\ominus}$;

A_3 is $-CH_2)_{\overline{s}}$; $-(CH_2)_2-N(CH_3)-(CH_2)_2-$; $-CH_2-C(CH_3)-CH_2-$ or

$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

where s is an integer from 2 to 6 inclusive.

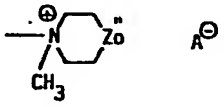
R_7'' is hydrogen, methyl or ethyl or

both R_7''s together with the N-atom to which they are attached form an unsubstituted morpholine, piperidine, pyrrolidine, piperazine or N-methyl piperazine ring.

R_8'' is methyl or ethyl; and

R_9'' is methyl, ethyl or benzyl; or

both R_8''s, R_9'' and the N-atom to which they are attached form a pyridine or picoline group (attached by the N-atom) or a group of formula



where Z_o'' is $-NH-$, $-O-$, $-CH_2-$,

$$-\underset{|}{N}(CH_3) \text{ or } -\underset{\oplus}{\underset{|}{N}}(CH_3)_2\,A^{\ominus}$$

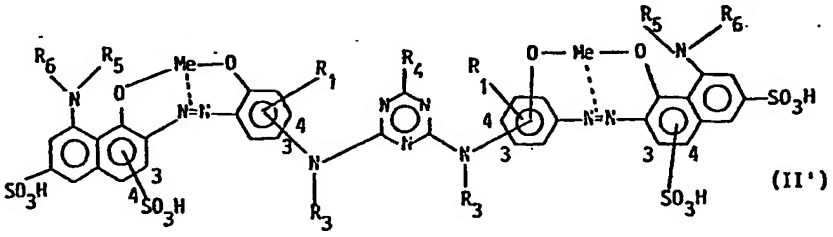
with the provisos:

i) that the sum of cationic and/or protonatable basic groups is greater than the sulpho and anionic groups present by at least one;

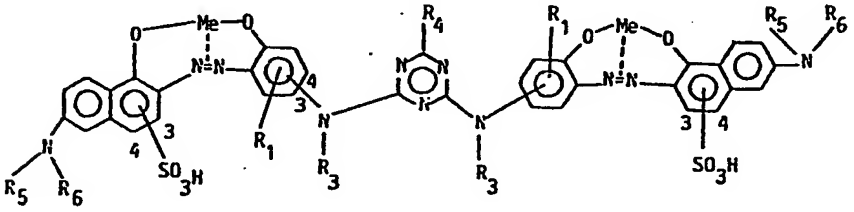
ii) that R_2'' and R_{4a}'' are not piperazine; and

iii) that R_1'' in the compounds of formula IIIa is in the 4- or 6-position shown.

4. A compound according to Claim 1 in free acid or acid addition salt form of formula II' or III'



(II')



(III')

where the symbols R_1, R_3-R_5 and R_6 are defined in Claim 1 M_e is a 1:1 or 1:2 complex forming metal atom with the provisos that:

i) in the compounds of formulae II' and III' the sum of cationic and protonatable basic groups exceeds the sum of sulpho and anionic groups by at least one;

ii) in the compounds of formula II' and III' in the floating sulpho groups are in the 3- or 4-position (shown);

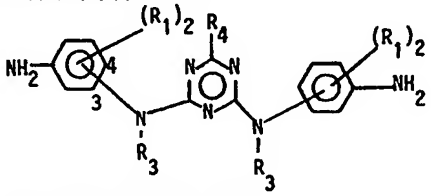
iii) in the compounds of formula II' and III' the floating groups $-NR_3'-$ are in the 3- or 4-position (shown);

iv) in the compounds of formula III' when both R_6s are the groups of formula a) and n is zero then the NR_3 groups are in the 3-position (shown).

5. A process of dyeing a substrate comprising applying to that substrate a compound according to any one of Claims 1 to 4.

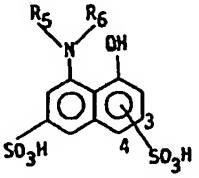
6. A substrate to which a compound according to any one of Claims 1 to 4.

7. A process for preparing a compound according to Claim 1 comprising reacting one mole of the tetrazotised compound of the formula X



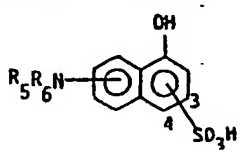
(X)

with 2 moles of a coupling component of formula XI



(XI)

or with 2 moles of a coupling component of formula XII



(XII)

where R_1 to R_8 are as defined in Claim 1;
or 1 mole of the coupling component of formula XI and 1 mole of the coupling component of the compound of formula XII.

8. A compound according to Claim 1 substantially as herein described with reference to any one of Examples 1 to 99.

9. A substrate when dyed by a process substantially as herein described with reference to any one of Dyeing Examples A to E.

10. A dyeing process substantially as herein described with reference to any one of Dyeing Examples A to E.

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